

TITLE: INVESTIGATION OF MIXED METAL SORBENT/CATALYSTS FOR THE SIMULTANEOUS REMOVAL OF SULFUR AND NITROGEN OXIDES

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Abstract

Simultaneous removal of SO₂ and NO_x using a regenerable solid sorbent will constitute an important improvement over the use of separate processes for the removal of these two pollutants from stack gases and possibly eliminate several shortcomings of the individual SO₂ and NO_x removal operations. Ceria-copper oxide sorbent/catalysts are expected to remove both SO₂ and NO_x from flue gases within a relatively wide temperature window, to produce significant amounts of elemental sulfur during regeneration, and to make it possible to use methane for the selective catalytic reduction of NO_x. Therefore, the objective of this research is to investigate SO₂ removal at lower temperatures by supported copper oxide-cerium oxide sorbents; conduct kinetic and parametric studies of the selective catalytic reduction of NO_x with NH₃ and CH₄ over alumina-supported cerium oxide and copper oxide-cerium oxide sorbent/catalysts; and investigate the possibility of elemental sulfur production during regeneration with CO or with CH₄-air mixtures.

The incipient wetness impregnation technique is used as the standard method for the preparation of the sorbents, using aqueous solutions of metal salts on an ALCOA alumina as support material. The resulting solid is dried in air at 393 K and calcined in nitrogen at 923 K for 6 hours. Since alumina plays an important role in sulfation, majority of sorbents are loaded at monolayer coverage of the support (which is about 10 wt% for 200 m²/g alumina). Copper oxide-cerium oxide sorbents were prepared by co-impregnation of nitrate salts of the metals. The physical properties of the sorbents are presented in Table 1:

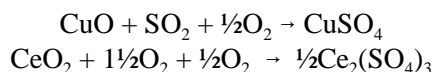
Table 1. Physical Properties of the Sorbents

Sorbent	Cerium Loading, mass %	Copper Loading, mass %	Surface Area, m ² /g
SOR10-II	4.58	5.54	122
SOR10-III	2.26	8.42	134
SOR10-IV	6.49	2.77	122
SOR10-V	1.90	8.76	130
SOR10-VI	0	10.36	105
SOR10-VII	10	0	126

For sulfation experiments, a CAHN instruments TG121 thermal analysis system is being used to record the weight of the sorbent as it undergoes sulfation. The weight and the sample temperature is monitored and stored

continuously using a microcomputer. Reactant gas mixture is prepared from high purity bottled gases without further purification. The first set of sulfation experiments are performed under standard sulfation conditions with temperature being varied from 723 to 823 K. The standard sulfation gas composition is 0.3% SO₂, 3% O₂, and balance N₂, the gas flow rate being 200 cc(NPT)/min. About 3 mg of sorbent particles in the 75-150 μm size range is used in each run. All the sorbents (SOR10-II to SOR 10-VII) have been crushed and sieved and the 75-150 μm range has been saved for sulfation experiments. It has been established that under these conditions mass transfer effects are negligible. First the effect of temperature on the sulfation of various sorbents was investigated; then five sulfation/regeneration cycles were run to establish the effect of cycling. Data obtained is being used to determine the intrinsic kinetics of the reactions and the sulfation capacity of the sorbents.

The following sulfation reactions take place on the sorbents consisting of ceria and copper oxide on alumina:



Since the selectivity of these two reactions is not known, the extent of sulfation, X_s, is represented by the ratio Δm/Δm_{max} where Δm=m-m_o, where m_o is the mass of the sorbent at the start of sulfation, and Δm_{max} is the maximum mass change due to the complete sulfation of copper and cerium oxides, calculated from the reaction stoichiometry of the two above-mentioned reactions and the composition and initial mass of the sorbent loaded to TGA. Conversion, X_s, is plotted as a function of time and these plots are used to compare the sorbents of different compositions and also the dependence of the performance of a sorbent on temperature. The conversion data will also be used to fit a reaction model with X_{ce} and X_{cu} as adjustable parameters to determine the selectivity of sulfation of the two sorbent constituents. At this time, the researchers are working on this model.

The results from the sulfation experiments show that the extent of sulfation on the sorbents increases as the cerium loading increases. Deep sulfation due to the sulfation of the support is more pronounced with sorbents containing more copper and increases with temperature.

Publications:

1. An abstract, submitted to the ISCRE 15 Conference to be held at Newport Beach, CA, on September 13-16, 1998, entitled "Behavior of Supported CuO/CeO₂ Sorbents under Sulfation Conditions" was accepted for presentation.
2. An abstract, submitted to the 15th Annual International Pittsburgh Coal Conference to be held at Pittsburgh, PA on September 14-18, 1998, entitled "Supported CuO/CeO₂ Sorbents for Gas Cleaning in Power Generation Systems" was accepted for presentation.
3. An abstract, entitled "Behavior of Supported Ceria/CuO Sorbents under Sulfation Conditions" was submitted to the 2nd World Congress on Environment to be held at Miami, FL in November 1998.
4. An abstract, entitled "Supported CuO/CeO₂ Sorbents for Combined Removal of SO₂ and NO_x from Flue Gases: NO_x Removal Characteristics" was submitted to the 2nd World Congress on Environment to be held at Miami, FL in November 1998.

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